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**Ion and Electron Interactions at Thermal
and Suprathermal Energies**

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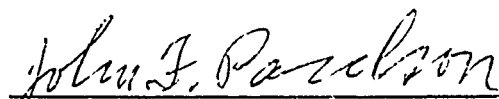
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13. ABSTRACT (Maximum 200 words) The flowing afterglow/Langmuir probe (FALP) apparatus has been used to study (a) electron attachment reactions of many species including, for the first time, some unstable molecular radicals, and some halogenated benzenes, triflate esters, halomethanes and haloethanes; (b) dissociative recombination reaction rate coefficients and, for the first time, the neutral products (specifically OH and H radicals) from the dissociative recombination of selected positive ions. The selected ion flow tube has been used to determine the rate coefficients and product ion distributions for many positive ion/neutral reactions, including reactions of ions in the series PH_n^+ ($n = 0$ to 4), of the rare gas ions Kr^+ , $Kr_2^{(H)+}$, Xe^+ and $Xe_2^{(H)+}$ and of the halogen ions F^+ , Cl^+ , Br^+ and I^+ . <i>Keywords:</i>				
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CONTENTS

Page Number

PREFACE

I	INTRODUCTION	1
II	SUMMARY OF RECENT RESULTS	3
III	CONCLUSIONS	4

REFERENCES REFERRED TO IN THE INTRODUCTION	6
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APPENDIX 1 SIFT AND FALP DETERMINATIONS OF IONIC REACTION RATE COEFFICIENTS	7
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APPENDIX 2 FORMATION OF Br_2^- IN THE REACTIONS OF THERMAL ELECTRONS WITH SOME BROMOMETHANES AND BROMOETHANES	20
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APPENDIX 3 FALP STUDIES OF THE PRODUCTS OF DISSOCIATIVE RECOMBINATION REACTIONS	32
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APPENDIX 4 SIFT STUDIES OF THE REACTIONS OF F^+ , Cl^+ , Br^+ AND I^+ AT 300K	40
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PREFACE

This work is part of a larger programme of ionic reaction studies at thermal energies conducted by the senior authors of this report. The overall programme includes studies of ion/neutral reactions, electron attachment, electron/ion recombination, ion/ion recombination and other plasma reaction processes. The work is largely intended as a contribution to the physics of natural plasmas, such as the ionosphere and the interstellar medium and of laboratory plasma media, such as gas laser systems, etchant plasmas and combustion plasmas. A great deal of relevant data has been obtained principally by exploiting the variable-temperature selected ion flow tube (VT-SIFT), the variable-temperature selected ion flow drift tube (VT-SIFDT) and the variable-temperature flowing afterglow/Langmuir probe (VT-FALP) techniques which were developed in our laboratory. Part of the overall programme is supported by a grant from the Science and Engineering Research Council.

We gratefully acknowledge the important contributions made to the various aspects of the work described in this report by Dr. C.R. Herd, Dr. C.A. Mayhew, Dr. J.F. Paulson, Dr. K. Giles and Mr. M.A. Geoghegan.

I INTRODUCTION

Our major commitment under the terms of the grant has been to study various gas-phase ionic reactions at thermal and near-thermal energies, with special reference to reactions that may occur in the terrestrial atmosphere and in combustion and discharge plasmas. Such reaction processes include (a) electron attachment (b) electron-ion recombination and (c) ion-neutral reactions. All these reaction processes can be studied using our selected ion flow drift tube (SIFDT) and Langmuir probe/flowing afterglow (FALP) apparatuses. Using these techniques, the rate coefficients and products for numerous reactions of the types referred to above have been determined. During the period covered by this report we have added laser and vacuum ultraviolet spectroscopic techniques to the very versatile FALP technique and this has allowed us to study the neutral products of some dissociative recombination reactions.

The results of the studies carried out during the first two years of the grant were presented in detail in the Interim Scientific Reports No 1 (dated 30th September 1988) and No 2 (dated 30th September 1989). This work has now been reported in several published papers given in the reference list to this report (references 1 - 11), and in summary is as follows:

(1) Electron Attachment

We have studied electron attachment reactions of the free radicals CCl_3 and CCl_2Br (ref 1), of $\text{C}_6\text{F}_5\text{Cl}$, $\text{C}_6\text{F}_5\text{Br}$ and $\text{C}_6\text{F}_5\text{I}$ (ref. 2), of $\text{CF}_3\text{SO}_3\text{CH}_3$ and $\text{CF}_3\text{SO}_3\text{C}_2\text{H}_5$ (ref 3) and of some haloethanes (ref. 4). In

most cases the rate coefficients for these reactions have been obtained at more than one temperature.

(ii) Positive Ion-Electron Dissociative Recombination

We have measured the dissociative recombination coefficients for several polyatomic ions at 300K (ref. 5) and summarised the FALP determination of dissociative recombination coefficients in a review paper (ref. 5). Following the addition of the laser and VUV spectroscopic techniques to the FALP, we studied quantitatively the production of OH radicals in the recombination of HCO_2^+ ions (ref. 7) and also for H_3O^+ and N_2OH^+ ions (ref. 8).

(iii) Ion-Neutral Reactions

We have determined accurately the relative proton affinities of H_2O , CS_2 and C_2H_4 (ref. 9) and carried out detailed studies at 300K of the reactions of ions in the series PH_n^+ ($n = 0$ to 4) with several molecular gases (ref. 10) and reactions of Kr^+ , Kr_2^+ , Xe^+ and Xe_2^+ with several molecular gases (ref. 11).

In the next section of this Final Scientific Report, we refer to the studies we have carried out during the third and final year of the grant period. Some details of these studies are given in Appendices 1 - 4 of this report.

II SUMMARY OF RECENT RESULTS

An overview of the SIFT and FALP work carried out in recent years is given in the review paper included as Appendix 1 to this report.

(a) Electron Attachment

The rate coefficients and product ions for the electron attachment reactions of CF_2Br_2 , CFBr_3 , $\text{CF}_2\text{BrCF}_2\text{Br}$, $\text{CH}_2\text{BrCH}_2\text{Br}$ and $\text{CH}_2\text{ClCH}_2\text{Br}$ have been determined at three temperatures. The interesting result obtained is that Br_2^- is a significant product of the CF_2Br_2 , CFBr_3 , $\text{CF}_2\text{BrCF}_2\text{Br}$ and $\text{CH}_2\text{BrCH}_2\text{Br}$ reactions along with Br^- (the major product in each reaction and at all three temperatures). Cl^- was the only observed product in the $\text{CH}_2\text{ClCH}_2\text{Br}$ reaction. The significance of these results is discussed in the paper included as Appendix 2 to this report.

(b) Positive Ion-Electron Dissociative Recombination

Following our pioneering work to determine the fractions of OH radicals released per recombining molecular ion, f_{OH} (see refs 7 and 8), we have now determined the fractions of H atoms released per recombining ion for some selected ions. This work was carried out in parallel with similar studies at The University of Rennes, France (B. Rowe and colleagues). The results of these pioneering studies are summarised in the short paper included as Appendix 3 to this report. The detailed results and further discussion will be given in a fuller paper at a later

date.

(c) Ion-Neutral Reactions

The rate coefficients and product ion distributions have been determined for the reactions of F^+ , Cl^+ , Br^+ and I^+ with some fifteen molecular gases using the SIFT at 300K. Several reaction processes are observed amongst these many reactions and the differing rate coefficients and product ions for these reactions are interpreted in terms of the recombination energies of the reactant ions, the ionization energies of the reactant molecules and the available electronic states in the product ions. The results of this study are summarised in the short paper included as Appendix 4 to this report. The detailed results will soon be reported in two major research papers.

III CONCLUSIONS

A great deal of progress has been made towards the objectives outlined in the original grant application. A large number of reactions have been studied in the three different categories viz (a) electron attachment (b) dissociative recombination and (c) ion-neutral reactions. These results are presented in some detail in the eleven papers given in the reference list (and referred to in the Introduction) and in the four appendices to this final report. Of special note are the first measurements of the attachment rate coefficients for molecular (unstable) free radicals and the first quantitative observations of OH and H radicals released in dissociative recombination of selected molecular ions. In all, the results obtained during the three years of the grant represent a

very significant contribution to the understanding of ionic and electronic interaction in gases at thermal energies.

REFERENCES REFERRED TO IN THE INTRODUCTION

- 1) Studies of Dissociative Electron Attachment to the Free Radicals CCl_3 and CCl_2Br using the FALP Apparatus.
N.G. Adams, D. Smith and C.R. Herd., Int.J. Mass Spectrom. Ion Processes, 84, 243, (1988)
- 2) FALP Studies of Electron Attachment Reactions of $\text{C}_6\text{F}_5\text{Cl}$, $\text{C}_6\text{F}_5\text{Br}$ and $\text{C}_6\text{F}_5\text{I}$.
C.R. Herd, N.G. Adams and D. Smith., Int.J. Mass Spectrom. Ion Processes, 87, 331, (1989)
- 3) A Study of Dissociative Electron Attachment to $\text{CF}_3\text{SO}_3\text{CH}_3$ and $\text{CF}_3\text{SO}_3\text{C}_2\text{H}_5$ Triflate Esters using the FALP Apparatus.
C.R. Herd, D. Smith and N.G. Adams., Int.J. Mass Spectrom. Ion Processes, 91, 177, (1989)
- 4) Studies of Dissociative Electron Attachment to some Haloethanes using the FALP Apparatus: Comparison with Data obtained using Non-Thermal Techniques.
D. Smith, C.R. Herd and N.G. Adams, Int.J. Mass Spectrom. Ion Processes, 93, 15, (1989)
- 5) Measurements of the Dissociative Recombination Coefficients for Several Polyatomic Ion Species at 300K.
N.G. Adams and D. Smith, Chem. Phys. Lett., 144, 11, (1988)
- 6) FALP Studies of Positive Ion/Electron Recombination
N.G. Adams and D. Smith. In "Dissociative Recombination: Theory, Experiment and Applications" Page 124, Editors J.B.A. Mitchell and S.L. Guberman, World Scientific Publishing, (1989)
- 7) Development of the Flowing Afterglow/Langmuir Probe Technique for Studying the Neutral Products of Dissociative Recombination using Spectroscopic Techniques: OH Production in the $\text{HCO}_2^+ + e$ reaction.
N.G. Adams, C.R. Herd and D. Smith, J. Chem. Phys., 91, 963, (1989)
- 8) OH Production in the Dissociative Recombination of H_3O^+ , HCO_2^+ and N_2OH^+ : Comparison with Theory and Interstellar Implications.
C.R. Herd, N.G. Adams and D. Smith, Astrophys. J., 349, 388, (1990)
- 9) Determination of the Relative Proton Affinities of H_2O and CS_2 relative to C_2H_4 .
B.J. McIntosh, N.G. Adams and D. Smith, Chem. Phys. Lett., 148, 142, (1988)
- 10) A Selected Ion Flow Tube Study of the Reactions of the PH_n^+ Ions ($n = 0$ to 4) with Several Molecular Gases at 300K.
D. Smith, B.J. McIntosh and N.G. Adams. J. Chem. Phys., 90, 6213 (1989)
- 11) Reactions of Kr^+ , Kr_2^+ , Xe , $^+\text{Xe}_2$ Ions with Several Molecular Gases at 300K.
K. Giles, N.G. Adams and D. Smith, J. Phys. B., 22, 873, (1989)

APPENDIX 1

SIFT AND FALP DETERMINATIONS OF
IONIC REACTION RATE COEFFICIENTS

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PROCEEDINGS OF THE XVI AIP
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SIFT AND FALP DETERMINATIONS OF IONIC REACTIONS RATE COEFFICIENTS

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A brief review is presented of some recent results of studies of ionic reactions at thermal energies using the selected ion flow tube (SIFT) and the flowing afterglow/Langmuir probe (FALP) techniques in our laboratory. From the SIFT results, we summarise the recent data on positive ion-molecule reactions, much of which relate to the synthesis of interstellar molecules. Thus, for example, data are discussed relating to the reactions of some hydrocarbon ions in the series $C_nH_m^+$, and phosphorus-bearing ions in the series PH_n^+ , which can lead to interstellar hydrocarbon and phosphorus-bearing molecules. From the FALP results, we summarise the data obtained on the rate coefficients for dissociative recombination, highlighting the recent work on the determination of the products of some dissociative recombination reactions, and discuss recent results on studies of dissociative electron attachment reactions. Reference is also made to our earlier studies of ion-ion mutual neutralization.

I. Introduction

Thermal and near-thermal energy reactions involving atomic and molecular species (neutral or ionized) and electrons occur in most ionized media, thus modifying the chemical composition of the media. In this sense, such ionic reactions are important in naturally-occurring ionized gases including the terrestrial atmospheric regions (the ionosphere, stratosphere and troposphere), other planetary atmospheres and interstellar gas clouds, and in laboratory plasmas such as gas lasers and surface etchant plasmas, and in electron capture detectors and atmospheric pollution monitors. The types of reactions that may occur include: (i) binary and ternary ion-molecule reactions, which convert positive ions and negative ions to chemically different ions and can also produce large cluster ions (especially at high ambient pressures and when polar molecules are present); (ii) electron attachment reactions which convert free electrons to

negative ions thus greatly modifying the physical and chemical characteristics of the ionized gas; (iii) positive ion-electron recombination which acts to return the ionized state to the neutral state and also creates new neutral species (often reactive radical species) in the gas; (iv) positive ion/negative ion mutual neutralization, which obviously removes ions of both sign of charge from the media and again generates new neutral species in the gas; (v) associative detachment reactions between negative ions and radicals (atoms or molecules) which release free electrons and form new neutral species. In the media mentioned above, most of these reaction processes will be occurring both sequentially and in parallel, usually amounting to a large number of individual reactions. Thus 'chemical evolution' of the media occur. For example, in the terrestrial stratosphere each of the processes (i) to (v) occur¹. However, there is yet no convincing evidence that negative ions are involved in the gas

phase ion chemistry which results in the production of the molecules observed in interstellar clouds (although there is a possible proviso to this which we mention later in Section 3.2(iii)). It should be mentioned also that reactions between neutral species (especially those involving neutral radical species) also occur in many ionized media and contribute to the gas phase chemical evolution of the media, but we will not be concerned with such reactions here.

The reasons for studying thermal energy ionic reactions is both to understand the fundamentals of the processes involved and also to provide critical data for inclusion in the complex ion-chemical models which have been constructed to describe the chemistry of ionized media. Much has been written about this topic and many comprehensive reviews are available ². In this paper, we are concerned specifically with the data obtained relating to the thermal energy ionic reaction processes (i) to (v) above, obtained using the extraordinarily versatile and productive selected ion flow tube (SIFT) ³ and flowing afterglow/Langmuir probe (FALP) ⁴ apparatuses developed and exploited in our laboratory. In particular, we discuss some of the most recent results we have obtained, most of which relate to reactions believed to occur in the terrestrial atmosphere and in interstellar gas clouds. Interest in these media has provided great stimulus to the study of ionic reactions at thermal energies.

2. The SIFT and the FALP Apparatuses

Both the SIFT and the FALP are fast flow tube experiments. They have been described in detail in some recent reviews ^{3,4}.

The SIFT apparatus was designed for the study of ion-neutral reactions under truly thermalised conditions. The principle of the technique is simple. Ions are created in an ion source, usually by electron impact on an appropriate source gas (however, several types of source have been used including flowing afterglows ⁵), mass selected

using a quadrupole mass filter and then injected through a venturi inlet into fast-flowing carrier gas (usually helium). These primary ions thermalise in multiple collisions with the carrier gas and are convected downstream where they are sampled via a pinhole orifice into a mass spectrometer/detection system. Reactant gases are introduced at a controlled flow rate into the thermalised swarm of ions and the resulting decrease in the primary ion signal to the downstream detection system and the detection of product ions of the reaction provide values for the rate coefficients and the product ion distributions for the reactions.

Measurements can be made at temperatures within the approximate range 80 to 600K. Reactions of positive ions and negative ions can be studied; indeed some thousands have been studied ^{6,7} involving a wide variety of reactant ions (including cluster ions) and reactant neutrals (including vapours, acids and atomic radicals). A variant on the SIFT, the selected ion flow drift tube (SIFDT), in which an accurately defined drift field is established along the length of the flow tube, allows measurement of rate coefficients for ion-neutral reactions at elevated centre-of-mass energies of the reactants ⁸. The SIFDT is providing an increasing amount of data, and comparisons with low energy beam data are being made. The SIFDT data find valuable application in modelling the chemistry of shocked regions of interstellar gas ⁹.

The FALP apparatus was designed for the study of plasma reaction processes, especially positive ion-electron recombination, ion-ion neutralization and electron attachment ^{10,11,12}. A flowing afterglow plasma is created by a microwave discharge in the upstream region of a fast flowing carrier gas. By virtue of the flow, ions and electrons are transported downstream and they relax from the suprathermal energies in the discharge to thermal energy in the downstream afterglow plasma. Again, helium is the most commonly used carrier gas and thus He^+ ions, electrons and metastable helium atoms He^m (both 2^1S and

2^3S) are transported into the afterglow. Also He_2^+ ions are created in three-body collisions involving He^+ ions and two He atoms (i.e. $\text{He}^+(2\text{He},\text{He})\text{He}_2^+$) and by associative ionization involving highly-excited He atoms (i.e. $\text{He}^*(\text{He},\text{e})\text{He}_2^+$). Chemical modification of the plasma can readily be achieved by the introduction of appropriate gases into the afterglow. For example, the addition of Ar removes both He^m (by the reaction $\text{He}^m(\text{Ar},\text{e})\text{Ar}^+$) and He_2^+ ions (by $\text{He}_2^+(\text{Ar},2\text{He})\text{Ar}^+$). A downstream mass spectrometer/detection system (standard to traditional flowing afterglow apparatuses) is included to monitor the ionic species (both positively- and negatively-charged) in the afterglow plasma.

The electron number density, n_e , can be determined at any position, z , along the axis of the afterglow plasma column using a movable Langmuir probe. The axial variation of n_e can be related to the nature and the speed of the loss processes for electrons. Thus, for example, a linear plot of $\ln n_e$ versus z is indicative of loss by ambipolar diffusion (as is the case for plasmas comprising atomic ions (He^+ , Ar^+) and electrons only)⁴. A linear plot of n_e^{-1} versus z is characteristic of plasmas in which loss of electrons is by dissociative recombination; such can be produced by adding molecular gases to the He^+/Ar^+ /electron plasma following which recombining molecular ions are produced by ion chemistry (e.g. $\text{Ar}^+(\text{O}_2,\text{Ar})\text{O}_2^+$). From such observations, dissociative recombination coefficients, α_e , can be obtained¹⁰. Similarly, the addition of electron attaching gases increases the z -gradient of n_e as electrons are converted to negative ions (e.g. $\text{e}(\text{CCl}_4,\text{CCl}_3)\text{Cl}^-$), and thus electron attachment coefficients, β , can be determined¹². If sufficient electron attaching gas is added to the afterglow plasma, all the free electrons are rapidly converted to negative ions and a positive ion-negative ion plasma is created. Then, using the Langmuir probe to determine the axial variation in the positive ion and/or negative ion number density (n_+ or n_-), ion-ion mutual neutralization rate

coefficients, α_i , can be determined¹¹.

The above briefly illustrates the range of processes that can be studied using the SIFT (ion swarm) and the FALP (afterglow plasma) methods. Using these techniques, most of the ionic and electronic processes that occur in low temperature ionized media can be studied. In combination they have been used to study dissociative attachment (FALP) and the reverse associative detachment (SIFT) reactions (e.g. $\text{e}(\text{HBr},\text{H})\text{Br}^-$; see Section 3.2(ii)). The value of SIFT experiments in assisting in understanding the ion chemistry occurring in the FALP experiments is great. For example, the ion molecule chemistry which occurs in the creation of specific afterglow plasmas for recombination studies can be understood by exploiting the SIFT apparatus. This has been useful in many ways, not least in the study of the recombination of a variety of protonated ions which are created by proton transfer from H_3^+ ions (e.g. $\text{H}_3^+(\text{CO}_2,\text{H}_2)\text{HCO}_2^+$)¹³ which we discuss briefly in Section 3.2(i). Finally, it cannot go unmentioned that the recent addition of laser and VUV spectroscopic diagnostics to the FALP experiment is now allowing the neutral products of dissociative recombination reactions to be determined. This major advance is reported briefly in Section 3.2(i).

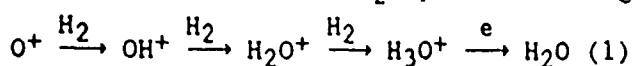
3. Some Recent SIFT and FALP Studies

As was previously mentioned, much of the SIFT and FALP work in our laboratory has been stimulated by our interest in interstellar chemistry, and a good deal of the new data discussed in this paper refer to interstellar reactions. Thus it is pertinent to mention here the elements of interstellar chemistry that are responsible for the synthesis of the wide variety of molecules that have been detected in interstellar clouds. Several recent reviews discuss this chemistry in some detail¹⁴.

Interstellar molecules are formed in the gas phase by many parallel and sequential binary positive ion-neutral reactions which generate a diversity of polyatomic ions. These ions can then

dissociatively recombine with free electrons to form the observed neutral molecules. The initial phases of this chemistry, starting from simple ions such as C^+ and H_3^+ , are now generally understood as is demonstrated by the reasonable agreement between the observed relative abundances of many interstellar molecular species and the predicted abundances based on ion-chemical models (see, for example, ref. 15). Such models required laboratory kinetic data for a large number of ion-neutral reactions and many of these data are now available; the lack of data relating to dissociative recombination reactions has been an inhibiting factor in this work until quite recently (see Section 3.2(1)).

Simple ion-molecule reaction sequences such as those which are usually considered to lead to H_2O production e.g.



and NH_3 production in interstellar clouds



are readily studied using the SIFT method. Generally, it is found that such reactions are rapid at room temperature 6,7. All three ion-molecule reactions in sequence (1) occur on every collision, i.e. the rate coefficients, k , for the reaction are equal to the collisional rate coefficient k_c 16. However, this cannot always be assumed to be the case, and indeed the first and the last reactions in sequence (2) are slow at 300K 17. More importantly, the k for these reactions vary greatly with temperature and when it is appreciated that the temperatures of interstellar clouds are very low (perhaps so low as 5K in some dense clouds, but more typically 20K) then it is important to obtain kinetic data at appropriately low temperatures. Currently, SIFT apparatuses are operated down to 80K and a good deal of valuable data have been obtained at this temperature 3,6. A very exciting new experiment (the so-called CRESU apparatus 18, which we refer to again below) can be operated down to 8K

and is now providing important data on ion-molecule reactions relevant to interstellar chemistry.

The ion-chemical routes to the production of some interstellar species are certain, especially those leading to the larger, polyatomic molecules such as the cyanopolyynes (HC_nN), and the larger hydrocarbons. This acts as the stimulus for further active laboratory studies as does the discovery of new interstellar molecules, such as the recent detection in the interstellar medium of the first phosphorus-bearing molecule, PN. 19 We refer to recent relevant SIFT work below.

As mentioned above, it is only recently with the advent of the FALP that data relating to the dissociative recombination of interstellar molecular ions have become available 13. Using the FALP, recombination coefficients for reactions such as the last in sequences (1) and (2) are readily obtained. A great uncertainty, however, is in the neutral products of such reactions; we refer briefly to very recent FALP studies on this in Section 3.2(1).

Before discussing particular SIFT and FALP studies, it must be reiterated that a stimulus for much of the work in our laboratory has also been interest in atmospheric reactions and in reactions occurring in laboratory plasmas 20. The FALP studies of electron attachment reactions and ion-ion mutual neutralization referred to below have been carried out in part with these applications in mind.

3.1 SIFT Results

In a short review such as this, which covers several types of processes, it is only possible to highlight a few of the more interesting recent results that have been obtained. Perhaps none is more interesting and significant to interstellar chemistry than the coordinated theoretical and experimental work that has shown that collisional rate coefficients, k_c , for ionic reactions involving polar reactant neutral molecules increase dramatically with decreasing temperature 21. The physical

reason for this is clear. The minimum potential energy path for ion-molecule reactions is a collinear neutral reactant dipole/ion trajectory and this is more readily achieved as the rotational excitation reduces (as the temperature reduces). Clary²² devised a procedure for calculating the rate coefficients for such reactions for reactant molecules in specific rotation states (the so-called ACCSA method) and in a co-ordinated SIFT study the proton transfer reactions of H_3^+ with HCN and HCl were studied over the temperature range 205 to 540K²¹. Excellent agreement was obtained between the theoretically predicted k_c and the experimentally measured k . Subsequent measurements of k for several reactions involving polar molecules at temperatures as low as 27K using the CRESU method have further demonstrated the validity of the theory¹⁸. Thus the general conclusion may be drawn that the k_c for reactions involving polar reactants (e.g. HCN, NH_3 , etc.) at the low temperatures of interstellar clouds ($\sim 20K$) greatly exceed their 300K values (typically $10^{-9} cm^3 s^{-1}$), reaching $\sim 10^{-7} cm^3 s^{-1}$ for very polar reactants at $\sim 20K$. This work has been reviewed quite recently by Clary²³. Recognition of this phenomenon provided the answer to a long standing problem in astrochemistry, i.e. the anomalously high abundance ratio of HCS^+ to CS in interstellar dense clouds²⁴. Because of the large dipole moment of CS the reaction $H_3^+(CS, H_2) HCS^+$ is now expected to proceed more rapidly than had previously been thought, thus enhancing the abundance of HCS^+ relative to CS.

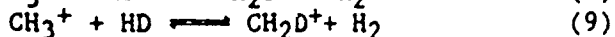
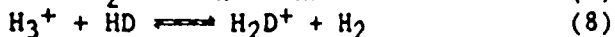
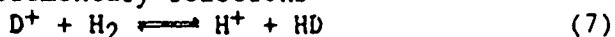
The abundance of HCS^+ in interstellar clouds is also enhanced due to the very large proton affinity (PA) of CS radicals²⁵. Proton transfer between neutral species is known to be facile for proton transfer reactions $XH^+(Y, X)YH^+$ when $PA(Y) > PA(X)$. It is therefore important to know the PA of a large number of neutral species in order to assess the loss rates of protonated species in real media such as interstellar gas clouds, the terrestrial stratosphere and laboratory plasmas. In this regard, the SIFT technique is especially valuable.

It is a straightforward procedure to inject particular protonated ions into the helium carrier gas, allow them to thermalise and then add a variety of neutral gases or vapours to the ion swarm, and observe whether or not proton transfer occurs from the ion to the reactant neutral. In this way, it can be ascertained if the PA(donor) is greater or less than the PA(acceptor) and thus a 'proton affinity ladder' can be constructed. The PA(CS) was determined to be $188.2 \pm 1 kcal mol^{-1}$ by this method²⁵, and very recently we have constructed an accurate PA ladder for the molecules CO (PA = $141.4 kcal mol^{-1}$), Br_2 , HBr, N_2O , HCl, Br, CH_4 and CO_2 ($128.5 kcal mol^{-1}$)²⁶. This work was greatly facilitated by studying proton transfer reactions at different temperatures, a feature essential for some of the other SIFT studies mentioned below.

A very large amount of data has been obtained relating to ionic reactions thought to occur in interstellar clouds notably using SIFT and ion cyclotron resonance (ICR) methods (see the data compilation by Ikezoe et al⁷). As a result of the skilled and often inspired work of those who construct and interpret the detailed models of interstellar clouds^{15,27}, the routes to many of the less complex interstellar molecules have been identified with reasonable certainty. The routes to the more complex molecules are, however, less certain principally because of the lack of laboratory data on reactions involving polyatomic species. Thus work on this goes on unabated. We have recently carried out a detailed survey of the reactions of the hydrocarbon ions in the series $C_nH_m^+$ ($n=4,5,6$; $m=0$ to 6) with H_2 and CO (the two most abundant molecules in dense interstellar clouds)²⁸, which represents the beginning of a determined effort to identify the routes to the production of polyatomic hydrocarbons in dense interstellar clouds. (Important work in this area has also been carried out by Bohme²⁹ and McElvany³⁰ and their colleagues). It is observed that generally only the very unsaturated ions in the series (i.e. $m < 2$) react with H_2 ,

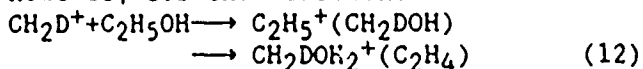
undergoing H-atom insertion e.g.
 $C_4^+, C_4H^+ + H_2 \longrightarrow C_4H^+, C_4H_2^+ + H$ (3)
 So hydrocarbon ions cannot become heavily hydrogenated by such reactions. Thus more saturated polyatomic hydrocarbon ions can only form from simple hydrocarbon ions in reactions with hydrocarbon molecules e.g.
 $C_3H_3^+ + C_2H_2 \longrightarrow C_5H_5^+ + h\nu$ (4)
 Reaction (4) is an example of a radiative association reaction, a process which is considered to be important in low temperature interstellar ion chemistry ³¹. In laboratory experiments, these reactions are generally observed to proceed via ternary association ^{6,32} e.g.
 $C_3H_3^+ + C_2H_2 + He \longrightarrow C_5H_5^+ + He$ (5)
 Such is the case for the reactions with CO of the highly unsaturated ions in the series $C_nH_m^+$, ²⁸ e.g.
 $C_4H^+ + CO + He \longrightarrow C_4HCO^+ + He$ (6)
 and we have shown that the radiative association analogue of these followed by electron-ion recombination could produce C_nO molecules such as C_3O which has been detected in interstellar clouds ³³. (Note it is assumed that the ion C_4HCO^+ formed in (6) could dissociatively recombine with an electron to form C_5O .)

One of the most interesting interstellar observations is that several molecular species are observed to be enriched in deuterium (relative to expectations based on the D/H cosmical abundance ratio) ³⁴. As a result of much careful SIFT work ³⁵, the suggestion first made by Watson ³⁶ that this enrichment is the result of isotope fractionation in ion-molecule reactions has been verified. Deuterium enhancement occurs in the elementary reactions



All these reactions proceed much faster to the right than to the left at low temperatures by virtue of the zero-point-energy differences between the reactants and products, and so (7) fractionates D into HD and (8), (9) and (10) fractionate D into H_2D^+ , CH_2D^+ and C_2HD^+ . Hence, the subsequent reactions of these ions can result in other molecules which are

enriched in deuterium. The rate coefficients for the forward and reverse of reactions (7), (8), (9) and (10) have been determined over significant temperature ranges using the SIFT and the enthalpy and entropy changes in the reactions have been determined ³⁵. Very recent SIFT studies in our laboratory of the reactions of H_3^+ , CH_3^+ and $C_2H_2^+$ and their deuterated analogues H_2D^+ , CH_2D^+ and C_2HD^+ are providing data also on the mechanisms of such ion-molecule reactions at thermal energies (a technique used to great effect also by others ³⁷). For example, these studies show that in the reaction of CH_2D^+ with CH_4 .



the D and the H atoms are quite equivalent and so the ratio of $C_2H_5^+$ and $C_2H_4D^+$ products are in accordance with simple statistical expectations. However, for the reaction:
 $CH_2D^+ + C_2H_5OH \longrightarrow C_2H_5^+(CH_2DOH)$
 $\longrightarrow CH_2DOH_2^+(C_2H_4) \quad (12)$
 the D atom remains bonded to the same carbon as it was before the reaction and D/H scrambling does not occur. Thus CH_2DOH is formed in reaction (12) but not CH_3OD . Such experiments are pointers to the deuterated molecules that may be produced and be detectable in interstellar clouds.

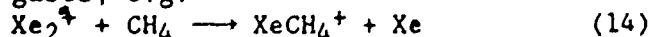
SIFT studies of reactions in recognisable series with many reactant gases have made valuable contributions to the understanding of the fundamentals of ion-molecule interactions as well as to interstellar chemistry. Thus we have previously studied in detail the reactions of ions in the series CH_n^+ , NH_n^+ , H_nCO^+ and H_nS^+ (for n from zero to the value appropriate to saturated ions in each case) ⁶ and these have indicated important routes to the synthesis of several interstellar molecules and greatly enhanced the understanding of the mechanisms of ion-molecule reactions. Recently we have studied the reactions of the ions derived from phosphine, i.e. the PH_n^+ ions (n = 0 to 4) with several molecular species most of which have been detected in interstellar clouds ³⁸. This work was stimulated by the recent detection of the first phosphorus-bearing

molecule, PN, in the interstellar medium¹⁹ and the desire to know how it was formed. The PH_n^+ ions are seen to be very reactive with most molecules (except, significantly, with H_2 and CO); the reactions with NH_3 produce PNH_2^+ and PNH_3^+ which on recombination with electrons could result in PN. The reactions of the PH_n^+ ions with hydrocarbons commonly generate organo-phosphorus ions which implies that organo-phosphorus molecules are probably present in interstellar gas (molecules like CP, HCP and HC_3P ; note that the analogous nitrogen-bearing molecules CN, HCN and HC_3N are abundant interstellar species). A subsequent study of the reactions of the protonated species PNH^+ , POH^+ , PSH^+ and H_2CP^+ has enabled the proton affinities of PN, PO, PS and HCP to be determined (by the method of bracketing outlined above)³⁹. The surprise result of this study was the large PA of PN ($-191 \pm 2 \text{ kcal mol}^{-1}$) which suggests that PNH^+ must surely co-exist with PN in interstellar gas, since PN will accept a proton from most protonated species, e.g.

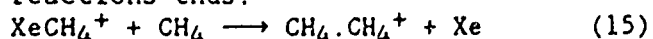
$$\text{H}_2\text{CN}^+ + \text{PN} \longrightarrow \text{PNH}^+ + \text{HCN} \quad (13)$$

Also, the large dipole moment of PN (-2.747 Debye)¹⁹ means that reactions like (13) will have large rate coefficients at low temperatures (again, following the ideas discussed at the beginning of this Section).

The versatility of the SIFT technique is clear; it can be used to study the reactions not only of ground state ions but also of metastable excited ions⁸. Following up earlier SIFT studies⁴⁰, we have studied the reactions of the spin-orbit states ($^2\text{P}_{3/2}$, $^2\text{P}_{1/2}$) of Kr^+ and Xe^+ and the reactions of the molecular ions Kr_2^+ and Xe_2^+ with a variety of molecules⁴¹. The molecular ions undergo facile switching reactions with many gases, e.g.

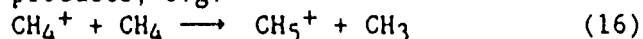


Further, the molecular product ions of these reactions undergo switching reactions thus:



generating the dimer ions, M_2^+ (in the above example M is CH_4). Such reactions have been observed also for $\text{M} = \text{H}_2\text{O}$, COS,

C_2H_2 , C_2H_6 , HCl, N_2O and CO⁴². The interest in these results is clear when it is appreciated that the M_2^+ dimer ions cannot generally be produced in the gas phase by association reactions of the M^+ ions with their parent molecule M, since such reactions usually result in other products, e.g.



However, some of the dimer ions e.g. $\text{H}_2\text{O}.\text{H}_2\text{O}^+$, $\text{HCl}^+.\text{HCl}$ etc. have been produced by ionizing the neutral dimers and their bond energies have been determined (see references in ref.42)..

All the above examples of recent SIFT studies refer to reactions between translationally-thermalised reactants. The inclusion of the drift field in the SIFT (creating a SIFDT) allows reactions between ions and neutrals to be studied at elevated centre-of-mass energies. SIFDT apparatuses are being exploited increasingly for such studies. A recent review describes some of this work⁹. Of note is the study of the $\text{C}^+(\text{H}_2, \text{H}) \text{CH}^+$ reaction⁴³ which is endothermic by 0.4 eV but which is initiated at elevated energies. This reaction is considered to be important in the shocked regions of interstellar gas⁴⁴. A comparison of the data on this reaction obtained using a SIFDT and low energy ion-neutral beam methods has been made^{9,43}. However, it must be remembered that the reactants in a SIFDT are not in thermal equilibrium. This feature has been exploited to study the influence of the rotational energy of the reactant neutral molecules on the efficiency of some ion-neutral reactions⁴⁵, studies which are difficult to envisage using other methods.

3.2 FALP Results

As mentioned above, the extraordinarily versatile FALP apparatus is currently being used to study (i) dissociative recombination; (ii) electron attachment and (iii) ion-ion mutual neutralization. We briefly discuss some of the recent studies of these processes in the order given.

(i) Dissociative Recombination

Prior to the FALP work in this area,

the most comprehensive study of dissociative recombination at thermal energies and the determination of recombination coefficients, α_e , had been achieved using the stationary afterglow (SA) technique ⁴⁶. Thus the α_e for some important atmospheric ions, including O_2^+ and NO^+ , had been determined over appreciable temperature ranges. The initial FALP studies of $\alpha_e(O_2^+)$ agreed well with the SA data both in magnitude and in the variation with temperature ($\alpha_e(O_2^+) \sim T^{-0.7}$) ¹⁰. However, an obvious disagreement between the FALP and SA data was apparent regarding the temperature dependence of $\alpha_e(NO^+)$ and this has since been resolved in favour of the FALP data and the data obtained using the trapped ion method ⁴⁷.

To date, the greatest value of the FALP in this area has been in the determination of the α_e for a number of interstellar positive ions ¹³. Most significant of all is that it has been shown that the most important interstellar ion H_3^+ in its ground vibronic state (from which much of interstellar chemistry begins) does not recombine at a measurable rate in binary collisions with electrons at and below room temperature (and even at 500K). Thus, under such conditions, the $\alpha_e(H_3^+)$ is very small at $\leq 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, a result in general accord with theoretical expectations ⁴⁸. (Note, however, that vibrationally-excited H_3^+ does indeed recombine rapidly ¹³). This quite unexpected result has great import to interstellar chemistry and is, of course, also of fundamental interest. A discussion of this and other $\alpha(H_3^+)$ data has been included in recent reviews ⁴⁹.

That H_3^+ does not recombine in the FALP plasma is of great practical value. H_3^+ /electron plasmas can be readily formed and then converted to plasmas comprising other protonated species, since proton transfer from H_3^+ to most other species is facile (because $PA(H_2)$ is small). Thus the addition of gases like, for example, CO and H_2O convert the H_3^+ plasma to HCO^+ and H_3O^+ plasmas via the proton transfer reactions $H_3^+(CO, H_2)HCO^+$ and $H_3^+(H_2O, H_2)H_3O^+$. In

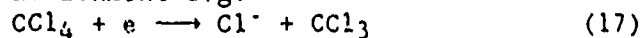
this way the α_e for a wide variety of protonated ions have been determined, many of interstellar importance, some over a range of temperature ^{13,50}. A significant practical point is that such studies are not possible using the SA technique, but are possible with the FALP because of the extraordinary chemical versatility of this fast flow tube method.

These kinetic data on α_e are vital to the proper understanding of molecular synthesis in interstellar clouds. Equally important is a knowledge of the neutral products of the dissociative recombination reactions of ground state polyatomic ions for which no data existed until quite recently. Now the FALP apparatus has been used in conjunction with LIF and VUV spectroscopic techniques to determine the fraction of OH radicals and H atoms produced in the dissociative recombination of H_3O^+ , HCO_2^+ , N_2OH^+ and O_2H^+ . The details of the experimental method are given in a very recent paper ⁵¹, and the detailed results and their interstellar significance is discussed in another recent paper ⁵². This exciting FALP/spectroscopy work is just beginning. It will be extended soon to probe the production of CN radicals in the recombination of CN-bearing ions; it also highlights the great value of the combination of the versatile FALP method and spectroscopy in studying ionic processes at thermal energies. The enormous potential of this powerful combination is clear. It is now being vigorously exploited in our laboratory.

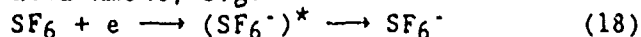
(ii) Electron Attachment

Electron attachment is an important process in ionized gases containing electronegative gases. It converts free electrons to negative ions and thus results in a change of the physical characteristics of the media (conductivity, dielectric constant etc.) and the ion chemistry occurring therein. This process is important in the lower terrestrial atmosphere, the negatively charged component of which is negative ions and not free electrons ¹. Electron attachment also plays an important role

in laboratory surface etchant plasmas ²⁰. Two distinct attachment processes have been recognised: (1) dissociative attachment e.g.

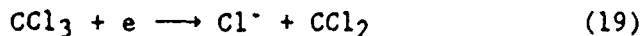


in which a negative ion and a free radical are formed, and direct attachment, e.g.



in which an excited negative ion of the parent molecule is formed which is relaxed either by radiation emission or collisional deactivation. Both (17) and (18) are fast, occurring essentially with unit efficiency (when $\beta \sim \beta_{\text{max}} \sim 3 \times 10^{-7} \text{cm}^3 \text{s}^{-1}$ at 300K) ¹².

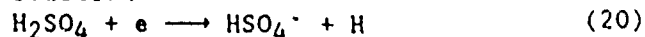
The FALP technique has proved to be ideal for the study of these attachment processes at thermal energies and attachment coefficients, β , have been measured over the approximate temperature range 200-600K for many reactions ⁵³. Generally speaking, the β for dissociative attachment reactions increase with increasing temperature (except when the reactions proceed very rapidly as is the case for reaction (17) and (18)) and then the FALP data provide values for the "activation energies" for the reactions ¹² ⁵³. The direct attachment process is not fully understood; occasionally the β actually decrease with increasing temperature for these reactions, as was recognised in the FALP experiment for the C_6F_6 reaction ⁵⁴. A very recent FALP discovery has been that the CCl_3 radicals formed in the "primary" dissociative attachment reaction (17) undergo rapid "secondary" dissociative attachment ⁵⁵ thus:



This has implications to the efficiency of electron capture detectors, and may commonly occur for molecular radicals containing halogen atoms (it certainly also occurs for CCl_2Br radicals ⁵⁵, but note that dissociative attachment to CCl_2 radicals is endothermic).

Dissociative electron attachment in the gas phase is analogous to Bronsted acid behaviour in the liquid phase. Thus strong Bronsted acids undergo rapid dissociative attachment, as a detailed FALP study has shown ⁵⁶. For example, the

reaction



is extremely rapid at 300K. Similarly, the 'superacids' FSO_3H and $\text{CF}_3\text{SO}_3\text{H}$ rapidly form the stable FSO_3^- and CF_3SO_3^- negative ions in reaction with thermal electrons. Gaseous HI is similarly 'acidic':



The FALP measurements have shown that the β for reaction (21) is $3 \times 10^{-7} \text{cm}^3 \text{s}^{-1}$ ⁵⁶. The reverse of these dissociative attachment reactions, in which a free electron is released and a new molecule formed, is known as associative detachment. Such reactions can be studied using the SIFT technique, and in a co-ordinated FALP and SIFT study, the forward and reverse reaction rate coefficients for reaction (21) and also for the analogous reactions involving HBr have been measured ⁵⁷. This has allowed the enthalpy and entropy changes in these reactions to be determined. The results obtained indicate that reaction (21) is essentially thermoneutral as expected from the known bond energy of HI molecules and the electron affinity of I atoms.

It must be stressed that using the FALP method, the β are determined under truly thermalised conditions at the particular temperature of the experiment. Thus by increasing the temperature, both the electron (translational) energy and the reactant molecule translational and internal energies are increased. This is not the case for the well-known drift tube and Krypton photoionization methods of determining β (referred to in ref 58) in which only the electron energy is usually varied. Therefore, not surprisingly, comparison of the results for these non-thermal experiments with those from FALP experiments must be approached with caution. We have attempted to clarify the differences to be expected in the measured β for some dissociative attachment reactions of haloethanes by thermal and non-thermal experiments in a recent paper ⁵⁸.

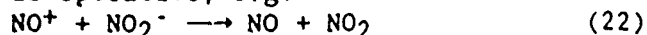
A final point worthy of note here is that in the study of numerous reactions

of halocarbon compounds (such as the Freons), atomic halogen negative ions are seen to be the only products of dissociative attachment reactions.

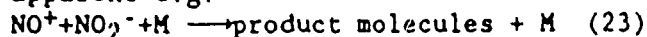
However, in our very recent FALP studies of some dibromoethanes (i.e. $(\text{CF}_2\text{Br})_2$, $(\text{CH}_2\text{Br})_2$, the molecular ion Br_2^- appears as a significant product (together with Br^-)⁵⁹. This observation bears some consideration and forcibly illustrates the importance of mass identification of the product ions of attachment reactions, a facility often not available in some experiments.

(iii) Positive Ion/Negative Ion Mutual Neutralization

This process, often termed ionic recombination, is important when negative ions form a significant fraction of the negatively-charged species in a plasma. Thus it plays an important role in limiting the ionization in the terrestrial stratosphere and troposphere¹. At low pressures, the binary process is operative, e.g.



but at higher pressures, collision-enhanced mutual neutralization and ternary ionic recombination become apparent e.g.

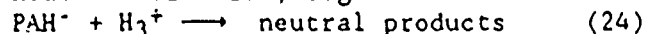


where M is a third body (in the lower atmosphere M would be N_2 or O_2). The FALP has been used to provide much of the reliable data on the binary process⁶⁰.

The binary ionic recombination coefficients, α_1 , have been determined for reactions involving (variously) simple and clustered molecular positive and negative ions. (Reaction (22) has been given considerable attention and the neutral products indicated (i.e. NO and NO_2) have been identified using emission spectroscopy⁶¹). The temperature dependence of the α_1 for this reaction has also been studied; thus $\alpha_1 \propto T^{-0.5}$ in accordance with theoretical expectations. A summary of some of the FALP work in this area is available¹¹.

Negative ions are not generally considered to be involved in interstellar chemistry. Recently, however, it has been proposed that negatively-charged

polycyclic aromatic hydrocarbons (PAH^-) may be present in dense clouds⁶². If this were so then mutual neutralization reactions with abundant positive ions (e.g. H_3^+ , HCO^+) could result in ionization loss and the production of neutral molecules, e.g.



At present this is somewhat speculative. It does, however, present another challenge to the FALP to provide data on such interesting reactions as (24).

4. Concluding Remarks

The above is merely intended to illustrate the versatility and productivity of the SIFT and FALP techniques in the study of gas phase ionic processes at or near thermal energies. Whilst much has been achieved using these techniques much more can yet be achieved by their continued exploitation. Currently both experiments operate in the low pressure regime (< 1 Torr). Developments are underway in our laboratory to extend our studies of ionic reactions to much higher pressures (up to atmospheric pressure). Undoubtedly, new reaction phenomena will be identified in higher pressure regimes, and a better understanding of the behaviour of practical devices such as electron capture detectors and plasma chromatography cells will be obtained.

Acknowledgments

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References

- ¹ D. Smith and N.G. Adams, in *Topics in Current Chemistry*, edited by S. Veprek and M. Venugopalan (Springer-Verlag, Heidelberg, 1980), Vol. 89, p.1.
- ² See for example the papers in *Swarms of Ions and Electrons in Gases*, edited by W. Lindinger, T.D. Mark and F. Howorka (Springer-Verlag, Vienna, 1984), and the references therein.
- ³ D. Smith and N.G. Adams, in *Gas Phase*

- Ion Chemistry*, edited by M.T. Bowers (Academic, New York, 1979), Vol.1, p.1.
- D. Smith and N.G. Adams, in *Advances in Atomic and Molecular Physics*, edited by D. Bates and B. Bederson (Academic, San Diego, 1987), Vol.24, p.1.
- 4 D. Smith, N.G. Adams, A.G. Dean, and M.J. Church, *J. Phys. D.* 8, 141, (1975).
N.G. Adams, M.J. Church and D. Smith, *J. Phys. D.* 8, 1409, (1975).
N.G. Adams and D. Smith, in *Techniques for the Study of Ion/Molecule Reactions*, edited by J.M. Farrar and W. Saunders Jr., (Wiley, New York, 1988), Vol. XX, p.165.
 - 5 D. Smith and N.G. Adams, *J. Phys. D.* 13, 1267, (1980).
 - 6 N.G. Adams and D. Smith, in *Reactions of Small Transient Species*, edited by M.A. Clyne and A. Fontijn (Academic, London, 1983), p.311.
 - 7 Y. Ikezoe, S. Matsuoka, M. Takebe and A.A. Viggiano, in *Gas Phase Ion-Molecule Reaction Rate Constants through 1986* (Maruzen Company Ltd., Tokyo, 1987).
 - 8 W. Lindinger and D. Smith, in *Reactions of Small Transient Species*, edited by M.A. Clyne and A. Fontijn, (Academic, London, 1983) p.387.
 - 9 D. Smith and N.G. Adams, in *Rate Coefficients in Astrochemistry*, edited by T.J. Millar and D.A. Williams, (Kluwer, Dordrecht, 1988), p.153.
 - 10 E. Alge, N.G. Adams and D. Smith, *J. Phys. B.* 16, 1433, (1983).
 - 11 D. Smith and N.G. Adams, in *Physics of Ion-Ion and Electron-Ion Collisions*, edited by F. Brouillard and J.W. McGowan (Plenum, New York, 1983), p.501.
 - 12 D. Smith, N.G. Adams and E. Alge, *J. Phys. B.* 17, 461 (1984).
 - 13 N.G. Adams, D. Smith, and E. Alge, *J. Chem. Phys.* 81, 1778, (1984).
 - 14 See papers in *Rate Coefficients in Astrochemistry*, edited by T.J. Millar and D.A. Williams (Kluwer, Dordrecht, 1988)
D. Smith, *Phil. Trans. R. Soc. Lond. A.* A323, 269, (1987).
 - D. Smith and N.G. Adams, *Faraday II.* (1989) in press.
 - 15 E. Herbst and C.M. Leung, *Ap. J. Suppl.*, (1989) in press.
 - 16 T. Su and M.T. Bowers, in *Gas Phase Ion Chemistry*, edited by M.T. Bowers, (Academic, New York, 1979) p.83.
 - 17 N.G. Adams and D. Smith, *Int. J. Mass Spectrom. Ion Proc.* 61, 133 (1984)
J.A. Luine and G.H. Dunn, *Ap. J. (Letters)* 299, L67 (1985).
 - 18 B.R. Rowe, in *Rate Coefficients in Astrochemistry*, edited by T.J. Millar and D.A. Williams (Kluwer, Dordrecht, 1988), p.153.
 - 19 L.M. Ziurys, *Ap. J. (Letters)* 321, L81 (1987).
 - 20 D. Smith and N.G. Adams, *Pure and Appl. Chem.* 56, 175 (1984).
 - 21 D.C. Clary, D. Smith and N.G. Adams, *Chem. Phys. Lett.*, 119, 320 (1985).
 - 22 D.C. Clary, *Mol. Phys.* 54, 605 (1985).
 - 23 D.C. Clary, in *Rate Coefficients in Astrochemistry*, edited by T.J. Millar and D.A. Williams (Kluwer, Dordrecht, 1988) p.1.
 - 24 T.J. Millar, N.G. Adams, D. Smith, and D.C. Clary, *Mon. Not. R. Astron. Soc.* 216, 1025 (1985).
 - 25 D. Smith, and N.G. Adams, *J. Phys. Chem.* 89, 3964 (1985).
 - 26 N.G. Adams, D. Smith, M. Tichy, G. Javahery, N.D. Twiddy, and E.E. Ferguson, *J. Chem. Phys.* (1989) in press.
 - 27 J.H. Black and A. Dalgarno, *Astrophys. Letts.* 15, 78 (1973).
T.J. Millar and A. Freeman, *Mon. Not. R. Astron. Soc.* 207, 405 (1984).
 - 28 K. Giles, N.G. Adams and D. Smith, *Int. J. Mass Spectrom. Ion Proc.*, 89, 303 (1989).
 - 29 D.K. Bohme, S. Dheandhanoo, S. Wlodek, and A.B. Raksit, *J. Phys. Chem.*, 91, 2569 (1987).
 - 30 S.W. McElvany, B.I. Dunlap, A. O'Keefe, *J. Chem. Phys.* 86, 715 (1987).
 - 31 D.R. Bates and F. Herbst, in *Rate Coefficients in Astrochemistry*, edited by T.J. Millar and D.A. Williams (Kluwer, Dordrecht, 1988) p.41.
 - 32 D. Smith, and N.G. Adams, *Int. J.*

- Mass Spectrom. Ion Proc. 76, 307 (1987).
- 33 E. Herbst, D. Smith and N.G. Adams, *Astron. Astrophys.* L13 (1984).
N.G. Adams, D. Smith, K. Giles and E. Herbst, *Astron. Astrophys.*, (1989) in press.
- 34 G. Winewisser, E. Churchwell and C.M. Walmsley, in *Modern Aspects of Microwave Spectroscopy*, edited by G.W. Chantry (Academic, New York, 1979), p.313.
- 35 D. Smith and N.G. Adams, in *Ionic Processes in the Gas Phase*, edited by M.A. Almoester-Ferreira (Reidel, Dordrecht, 1984) p.41.
- 36 W.D. Watson, in *Topics in Interstellar Matter*, edited by H. van Woerden (Reidel, Dordrecht, 1977) p.135.
- 37 C.H. DePuy, in *Ionic Processes in the Gas Phase*, edited by M.A. Almoester-Ferreira (Reidel, Dordrecht, 1984) p.227.
- 38 D. Smith, B.J. McIntosh and N.G. Adams, *J. Chem. Phys.* 90, 6213 (1989).
- 39 Paper in preparation.
- 40 N.G. Adams, D. Smith, and E. Alge, *J. Phys. B.* 13, 3235 (1980).
- 41 K. Giles, N.G. Adams and D. Smith, *J. Phys. B.* 22, 873 (1989).
- 42 D. Smith, and N.G. Adams, *Chem. Phys. Lett.* (1989) in press.
- 43 N.D. Twiddy, A. Mohebbati, and M. Tichy, *Int. J. Mass Spectrom. Ion Proc.* 74, 251 (1986).
- 44 M. Elitzur, and W. D. Watson, *Ap. J.* 236, 172 (1980).
- 45 N.G. Adams, D. Smith and E.E. Ferguson, *Int. J. Mass Spectrom. Ion Proc.* 67, 67 (1985).
N.G. Adams and D. Smith, *Int. J. Mass Spectrom. Ion Proc.* 81, 273 (1987).
A.A. Viggiano, R. A. Morris, F. Dale, J.F. Paulson, K. Giles, D. Smith and T. Su, *J. Chem. Phys.* (1989) in press.
- 46 J.N. Bardsley and N.A. Biondi, *Adv. Atom. Mol. Phys.* 6, 1 (1970).
- 47 R. Johnsen, *Int. J. Mass Spectrom. Ion Proc.* 81, 67 (1987).
- 48 H.H. Michels and R.H. Hobbs, *Ap. J. (Letters)* 286, L27 (1984).
- 49 N.G. Adams and D. Smith in *Rate Coefficients in Astrochemistry*, edited by T.J. Millar and D.A. Williams (Kluwer, Dordrecht, 1988) p.173.
N.G. Adams and D. Smith, in *Dissociative Recombination: Theory, Experiment and Applications*, edited by J.B.A. Mitchell and S.L. Guberman (World Scientific, Singapore, 1989).
- 50 N.G. Adams and D. Smith, *Chem. Phys. Lett.* 144, 11 (1988).
- 51 N.G. Adams, C.R. Herd and D. Smith, *J. Chem. Phys.* (1989) in press.
- 52 C.R. Herd, N.G. Adams and D. Smith, *Ap. J.* (1989) in press.
- 53 E. Alge, N.G. Adams, and D. Smith, *J. Phys. B.* 17, 3827 (1984).
- 54 N.G. Adams, D. Smith, E. Alge, and J. Burdon, *Chem. Phys. Lett.* 116, 460 (1985).
- 55 N.G. Adams, D. Smith, and C.R. Herd, *Int. J. Mass Spectrom. Ion Proc.* 184, 243 (1988).
- 56 N.G. Adams, D. Smith, A.A. Viggiano, J.F. Paulson, and M.J. Henchman, *J. Chem. Phys.* 84, 6728 (1986).
- 57 D. Smith and N.G. Adams, *J. Phys. B.* 20, 4903 (1987).
- 58 D. Smith, C.R. Herd and N.G. Adams, *Int. J. Mass Spectrom. Ion Proc.* (1989) in press.
- 59 Paper in preparation.
- 60 D. Smith and M.J. Church, *Int. J. Mass Spectrom. Ion Proc.* 19, 185 (1976).
D. Smith, M.J. Church and T.M. Miller, *J. Chem. Phys.* 68, 1224 (1978).
M.J. Church and D. Smith, *J. Phys. D.* 11, 2199 (1978).
- 61 D. Smith, N.G. Adams and M.J. Church, *J. Phys. B.* 11, 4041 (1978).
- 62 A. Omont, *Astron. Astrophys.* 164, 159 (1986).
S. Lepp and A. Dalgarno, *Ap. J.* 324, 553 (1988).

APPENDIX 2

FORMATION OF Br_2^- IN THE REACTIONS
OF THERMAL ELECTRONS WITH SOME BROMOMETHANES
AND BROMOETHANES

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INT.J.MASS SPECTROM. ION PROCESSES, 96, 341, (1990)

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FORMATION OF Br_2^- IN THE REACTIONS OF THERMAL ELECTRONS WITH

SOME BROMOMETHANES AND BROMOETHANES

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Short Title: Br_2^- Production in Dissociative Attachment

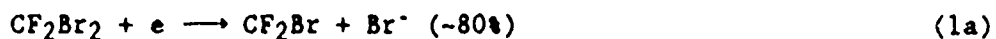
ABSTRACT

Following the recent report that Br_2^- ions (together with Br^- ions) are observed as products in the dissociative attachment reaction of electrons with CF_2Br_2 as studied using the Krypton photoionization method, we have studied the attachment reactions of CF_2Br_2 , CFBr_3 , $\text{CF}_2\text{BrCF}_2\text{Br}$, $\text{CH}_2\text{BrCH}_2\text{Br}$ and $\text{CH}_2\text{ClCH}_2\text{Br}$ using the FALP technique at 298, 380, 475K with a helium bath gas pressure of about 1 Torr. It was confirmed that Br_2^- is indeed a product of the CF_2Br_2 reaction and that it is also a significant product of the CFBr_3 , $\text{CF}_2\text{BrCF}_2\text{Br}$ and $\text{CH}_2\text{BrCH}_2\text{Br}$ reactions along with the major product ion Br^- . The production of Br_2^- is briefly discussed and it is speculated that the $\text{Br}_2^-/\text{Br}^-$ product ratio may be larger at higher bath gas pressures which are used in electron capture detectors.

INTRODUCTION

In the study of dissociative electron attachment reactions of halogenated aliphatic hydrocarbons at thermal energies, an atomic halide ion is almost invariably observed to be the only product ion [1,2]. For monosubstituted species, e.g. CH_3Br , this is not surprising since at thermal energies no combination of products other than the halide negative ion and CH_3 can render dissociative attachment energetically possible (e.g. CH_3^- and the halogen atom cannot be produced). For dibromomethane, CH_2Br_2 , again Br^- is the only observed product ion [3,4], even though Br_2^- is a stable negative ion, but production of Br_2^- may be endothermic. Unfortunately, the ergicities of these reactions cannot be ascertained with any certainty because the required thermochemical data are not available. It is noteworthy that in the thermal dissociative attachment reactions of the chlorinated methanes CH_2Cl_2 , CHCl_3 and CCl_4 , no Cl_2^- is observed and the only product ion is Cl^- [2].

Recently, Alajajian et al [4], using their Krypton photoionization method, have observed Br_2^- as well as Br^- in the dissociative attachment reaction



As far as we are aware this is the first example of the production of molecular halogen negative ions in the thermal energy attachment reactions of halogenated hydrocarbons. We therefore decided to study reaction (1) using our flowing afterglow/Langmuir probe (FALP) apparatus [2,5] which we have previously used to study many attachment reactions in the thermal energy regime, some over appreciable temperature ranges [5]. This study was extended to include attachment reactions of other bromomethanes and bromoethanes to determine whether Br_2^- ions (or any other molecular negative ions) were formed in these reactions. Some of

these brominated hydrocarbons are known atmospheric pollutants [6] and there is an obvious need to understand more of their chemistry.

EXPERIMENTAL

The FALP apparatus and the technique used for attachment studies have been described in detail previously [2,7]. It is sufficient to say here that a thermalised flowing afterglow plasma is created downstream of a microwave discharge in helium, attaching gases are added in controlled amounts into the plasma and then the electron number density (n_e) along the afterglow column (along the z-axis) is determined using a movable Langmuir probe. The attachment coefficients, β , are determined by analysing the n_e versus z curves as described in a previous publication [7]. The product ions of the reactions are identified using a downstream quadrupole mass spectrometer operated at low resolution in order to minimise mass discrimination. This is particularly important in the determination of $\text{Br}^-/\text{Br}_2^-$ product ratios because of the large mass difference between these ions. The gases included in this study were CF_2Br_2 , CFBr_3 , $\text{CF}_2\text{BrCF}_2\text{Br}$, $\text{CH}_2\text{BrCH}_2\text{Br}$ and $\text{CH}_2\text{ClCH}_2\text{Br}$. Measurements were made at gas temperatures of 298, 380 and 475 K. In order to facilitate the accurate determination of the very small flow rates of attaching gases, they were introduced as accurately known dilute mixtures (-1 to 10%) in pure helium as previously described [2,3,7]. The error in the β values is considered to be $\pm 25\%$, although the relative values of the β for the various reactions are more accurate ($\pm 15\%$).

RESULTS

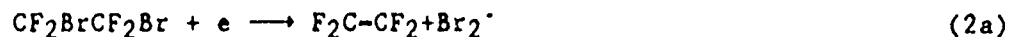
The β values and the product ion distributions (in percent) obtained at the three temperatures are listed in Table 1. An interesting result is that Br_2^- is indeed a significant product of the CF_2Br_2 reaction,

confirming the result obtained using the Krypton photoionization method [4]. Br_2^- is also a product of the CFBr_3 , $\text{CF}_2\text{BrCF}_2\text{Br}$ and $\text{CH}_2\text{BrCH}_2\text{Br}$ reactions. Because the β for the CF_2Br_2 reaction at 298K is close to the maximum value of β (i.e. β_{max} , according to s-wave capture theory [8]), and reaches β_{max} at 475K (see Fig.1) with Br_2^- comprising ~15% of the products at each temperature, then Br_2^- production (reaction (1b)) is surely exothermic not endothermic (see the INTRODUCTION).

Several features of the data in Table 1 deserve comment. The rate coefficient for the CFBr_3 reaction at 298K is much smaller than that for the CF_2Br_2 reaction at the same temperature and increases only slowly with temperature. From the Arrhenius-type plot in Fig.1, an 'activation energy', E_a , of about 48 meV is obtained for the CFBr_3 reaction (a typical value for many dissociative attachment reactions [2,3]). Also interesting is the fact that Br_2^- is a smaller percentage of the product distribution for CFBr_3 (~8%) than it is for CF_2Br_2 (~14%), even though on the basis of simple statistics the reverse would be expected. Clearly, such a simple approach to the interpretation of the data obtained for these reactions, even for such chemically similar compounds, is unprofitable. However, it is clear that again Br_2^- production cannot be significantly endothermic even though the β are relatively small (it is conceivable that the endothermicity of the CFBr_3 reaction could be of the order of E_a i.e. ~48 meV). The features of these reactions (i.e. the β , temperature dependences and product distributions, etc.) are likely to be controlled by the detailed forms of the potential surfaces on which the reactions proceed.

In the very rapid dissociative attachment reaction of $\text{CF}_2\text{BrCF}_2\text{Br}$, about 15% of the product ions are Br_2^- , whereas for the slower $\text{CH}_2\text{BrCH}_2\text{Br}$ reaction only about 3% of the product ions are Br_2^- . Even within the uncertainties of the ergicities of these reactions there are clearly

defined exothermic channels for Br_2^- production in these reactions if ethene-like double-bonded products are formed, e.g.



Indeed, in reaction (2) the channel (2b) producing Br^- and Br is probably exothermic also; perhaps Br^- is produced partly by the dissociation of excited $(\text{Br}_2^-)^*$ as well as by reaction (2c). Note that the β for the slower $\text{CH}_2\text{BrCH}_2\text{Br}$ reaction increases with temperature according to the Arrhenius law (see Fig. 1) and that an E_a of ~ 70 meV is appropriate to that reaction (see Table 1).

In the reaction of $\text{CH}_2\text{ClCH}_2\text{Br}$, only the atomic ions Br^- and Cl^- were observed as products (Br^- being the majority product at each temperature; see Table 1). It is, however, conceivable that the reaction could proceed to produce excited $(\text{BrCl}^-)^*$ ions which all dissociate to atomic products Cl^-/Br and/or Br^-/Cl in ratios depending on the temperature, carrier gas pressure, etc. Note that the β values for this reaction are small. From the Arrhenius plot of the data in Figure 1, a large E_a of 156 meV is obtained.

DISCUSSION AND CONCLUSION

The production of Br_2^- in the dissociative attachment reactions of molecules in which the bromine atoms are bonded to different carbon atoms was somewhat unexpected, but it occurs in several reactions. Presumably, the reactions proceed firstly by the formation of a short-lived, vibrationally-excited parent negative ion. The single carbon-carbon bond is then bridged temporarily to form Br_2^- and, after elimination of the Br_2^- , an additional Π -bond is formed in the product $\text{H}_2\text{C}=\text{CH}_2$ (and $\text{F}_2\text{C}=\text{CF}_2$) molecules. The presence of the Br (and F) atoms in the

attaching molecules presumably inhibits free rotation around the C-C bond resulting in trans and gauche forms of the molecules, and this might limit the fraction of Br_2^- (relative to Br^-) that can be formed.

The present studies were carried out in helium bath gas at a pressure of about 1 Torr. It is interesting to speculate as to how the $\text{Br}^-/\text{Br}_2^-$ product ratio might be influenced by higher bath gas pressures. If Br_2^- is indeed formed initially in an excited state, a fraction of which dissociate, then one might expect that collisions of $(\text{Br}_2^-)^*$ with bath gas atoms would remove excitation energy and thus minimise dissociation to Br^- and Br . Thus the fraction of Br_2^- would increase at higher bath gas pressures such as are characteristic of electron capture detectors [9].

Acknowledgment

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REFERENCES

- 1 L.G. Christophorou, Atomic and Molecular Radiation Physics, Wiley-Interscience, London, 1971.
- 2 D. Smith, N.G. Adams and E. Alge, J. Phys. B, 17 (1984) 461.
- 3 E. Alge, N.G. Adams and D. Smith, J. Phys. B, 17 (1984) 3827.
- 4 S.H. Alajajian, M.T. Bernius and A. Chutjian, J. Phys. B, 21 (1988) 4021
- 5 D. Smith and N.G. Adams, in W. Lindinger, T.D. Mark and F. Howorka (Eds.), Swarms of Ions and Electrons in Gases, Springer-Verlag, Vienna, 1984, p.284.
- 6 R.P. Wayne, Chemistry of Atmospheres, Clarendon Press, Oxford, 1985.
- 7 N.G. Adams, D. Smith and C.R. Herd, Int. J. Mass Spectrom. Ion Processes, 84 (1988) 243.
- 8 J.M. Warman and M.C. Sauer Jr., Intern. J. Radiat. Phys. Chem., 3 (1971) 273; A.A. Christodoulides, L.G. Christophorou, R.Y. Pai and C.M. Young, J. Chem. Phys. 70 (1979) 1156.
- 9 R.S. Mock, D.R. Zook and E.P. Grimsrud, Int. J. Mass Spectrom. Ion Processes, 91 (1989) 327.

TABLE 1

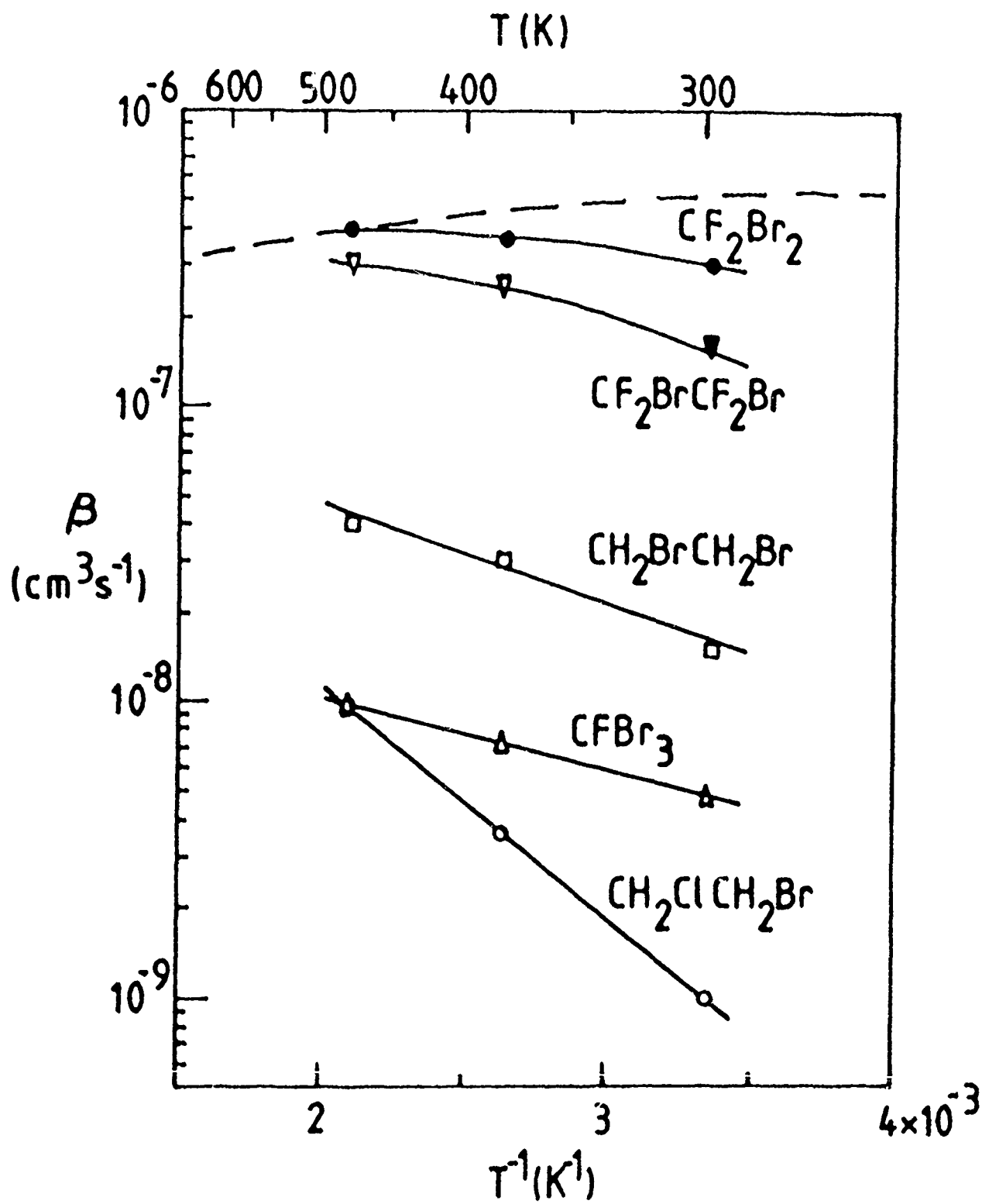
Rate coefficients, β , (cm^3s^{-1}) and product ion distributions, R, (%) for electron attachment to some bromomethanes and bromoethanes at the temperature indicated. The activation energies, E_a , (meV) as deduced from the slopes of the Arrhenius plots in Fig.1 are also included.

Reactant	298K		380K		475K		E_a
Molecule							(meV)
	β	R	β	R	β	R	
CF ₂ Br ₂	3.0(-7)	Br ⁻ (85%)	3.7(-7)	Br ⁻ (87%)	4.0(-7)	Br ⁻ (86%)	-
		Br ₂ ⁻ (15%)		Br ₂ ⁻ (13%)		Br ₂ ⁻ (14%)	
CFBr ₃	4.8(-9)	Br ⁻ (91%)	7.4(-9)	Br ⁻ (92%)	9.6(-9)	Br ⁻ (95%)	48
		Br ₂ ⁻ (9%)		Br ₂ ⁻ (8%)		Br ₂ ⁻ (5%)	
CF ₂ BrCF ₂ Br	1.6(-7)	Br ⁻ (80%)	2.5(-7)	Br ⁻ (85%)	3.0(-7)	Br ⁻ (90%)	<44
		Br ₂ ⁻ (20%)		Br ₂ ⁻ (15%)		Br ₂ ⁻ (10%)	
CH ₂ BrCH ₂ Br	1.5(-8)	Br ⁻ (97%)	3.1(-8)	Br ⁻ (97%)	4.1(-8)	Br ⁻ (97%)	70
		Br ₂ ⁻ (3%)		Br ₂ ⁻ (3%)		Br ₂ ⁻ (3%)	
CH ₂ ClCH ₂ Br	1.0(-9)	Br ⁻ (80%)	3.6(-9)	Br ⁻ (70%)	9.7(-9)	Br ⁻ (>70%)	156
		Cl ⁻ (20%)		Cl ⁻ (30%)		Cl ⁻ (<30%)	

FIGURE CAPTION

Fig. 1 Arrhenius plots (β versus T^{-1}) for the attachment reactions of electrons with the molecules indicated from the slopes of which activation energies, E_a , have been derived (see Table 1). The dashed line represents the maximum values of β (β_{\max}) deduced using s-wave capture theory [8].

Fig. 1



APPENDIX 3

FALP STUDIES OF THE PRODUCTS
OF DISSOCIATIVE RECOMBINATION REACTIONS

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AND M.A. GEOGHEGAN

SYMPOSIUM ON ATOMIC AND SURFACE PHYSICS,
OBERTRAUN, AUSTRIA, MARCH 1990. P.57

FALP Studies of the Products of Dissociative Recombination Reactions

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Abstract: The FALP technique has recently been extended to include laser induced fluorescence and vacuum ultraviolet spectroscopic diagnostics. Now, the neutral products of some dissociative recombination reactions can be determined. Thus we have obtained values for the fractions of OH radicals (f_{OH}) and H atoms (f_H) released per recombining ion for selected recombining ground state polyatomic ions.

1. Introduction

Dissociative recombination of molecular positive ions with electrons is an important loss process for ionization and for the production of new neutral species in most ionized gases and cold plasmas. The neutral species produced by this process may be stable, relatively unreactive molecules or very reactive radicals (atomic or molecular). In order to understand the complex ion chemistry of media such as laboratory plasmas (e.g. laser and etchant plasmas) and natural plasmas such as the terrestrial ionosphere and interstellar gas clouds, a great deal of data are required relating to ion/molecule reactions, electron attachment, ion-ion mutual neutralization and dissociative recombination. Specifically, the rate coefficients and the products of many such reactions are required. In this paper we are concerned with recent determinations of the rate coefficients, α_g , and, more particularly, the neutral products of some dissociative recombination reactions which have been made using our flowing afterglow/Langmuir probe (FALP) technique. We have been exploiting the FALP apparatus for a few years to determine the α_g for particular reactions. Now, quite recently, we have added laser induced fluorescence (LIF) and vacuum ultraviolet (VUV) spectroscopic techniques to the FALP apparatus and thus made possible the determination of some of the neutral products of the dissociative recombination reactions of ions in their ground vibronic states at 300K, including the known interstellar ions H_3O^+ , HCO_2^+ and H_2CN^+ . This work, in part, is being carried out in collaboration with the University of Rennes, France (B.R. Rowe and colleagues).

2. Experimental

The basic FALP apparatus has been described in detail previously [1]. Briefly, thermalised flowing afterglow plasmas are produced along a flow tube by creating a microwave discharge upstream in the carrier gas (helium); the species in this plasma are He^+ and He_2^+ ions, electrons and He metastable atoms (He^{m}); the He^{m} are destroyed by introducing argon into the afterglow thus creating more electrons and Ar^+ ions (Penning ionization). The He_2^+ ions are also destroyed by the Ar atoms, again creating Ar^+ ions. The $\text{He}^+/\text{Ar}^+/\text{electron}$ plasma so formed decays slowly by ambipolar diffusion. A measurement of the electron number density, n_e , along the flow tube axis, z , using the movable Langmuir probe confirms this (a linear plot of $\ln n_e$ versus z being the confirmation). The addition of appropriate molecular gases to this plasma converts the non-recombining atomic ions to recombining molecular ions (e.g. the addition of O_2 creates an $\text{O}_2^+/\text{electron}$ plasma) and then a rapid decrease in n_e along z occurs. A plot of n_e^{-1} versus z is then linear and the slope of the plot provides a value of α_e . The α_e for many reactions have been determined in this way [1,2,3].

A particularly profitable approach to the determination of the α_e for many reactions has been the following. By operating the experiment at a high helium carrier gas pressure (~1.2 torr is appropriate), most of the He^+ ions are converted to He_2^+ ions in the upstream region; then the addition of H_2 to the afterglow plasma converts He_2^+ and He^{m} to H_2^+ which rapidly react with H_2 to form H_3^+ . We have shown [2,4] that H_3^+ in its ground state does not recombine with electrons at a significant rate, (a remarkable result from the viewpoint of interstellar chemistry), and a plot of $\ln n_e$ versus z in the $\text{H}_3^+/\text{electron}$ plasma confirms that ambipolar diffusion is the only significant loss process. The addition of almost any gas, M, to this plasma results in the rapid production of MH^+ ions (via the proton transfer reaction of H_3^+ with M) and hence $\text{MH}^+/\text{electron}$ plasmas. Then the α_e for the $\text{MH}^+ + e$ reactions can be readily determined. In this way, the α_e for many protonated species have been determined, including those for some important interstellar ions (e.g. HCO^+ , N_2H^+ , H_3O^+ , H_2CN^+ , etc.) [2,3,5].

As was mentioned in the Introduction, VUV and LIF spectroscopic diagnostics (and also an optical monochromator) have been added to the versatile FALP apparatus. This allows the study of light emission (and absorption) and fluorescence from a variety of reaction processes. In

order to determine quantitatively the branching ratios of H atoms and OH radicals produced in some dissociative recombination reactions, the following procedure was adopted.

A helium microwave discharge was used as a source of Lyman- α radiation which was directed across the diameter of the flow tube in the downstream region and received by the slit of a VUV spectrometer tuned to the L_{α} wavelength. H atoms were generated in the helium carrier gas by passing H_2 through the upstream microwave cavity. Thus H atoms were convected downstream and detected by determining the fractional absorption of the L_{α} radiation. The absolute H atom number densities so determined were $\sim 10^{11} \text{ cm}^{-3}$. The details of this work are given in a recent paper [6]. The addition of sufficient NO_2 to this H atom swarm converts all the H atoms to OH radicals via the reaction $H + NO_2 \longrightarrow OH(v) + NO$. Any OH radicals generated in vibrationally excited states (v) are rapidly quenched to the ground state in collisions with NO_2 . The OH(v=0) are then detected using the LIF facility. Thus laser light at $\sim 281 \text{ nm}$ is directed into the flow tube and excites OH molecules in the (X,v=0) state to the (A,v=1) state and the fluorescence at $\sim 312 \text{ nm}$ due to (A,v=1) to (X,v=1) transitions is detected using a filtered photomultiplier. The intensity of the LIF at a particular rovibronic wavelength is correlated with the absolute H atom number density, [H], as determined using the VUV experiment and thus a calibration of the absolute OH number density, [OH], is obtained. Further details are given in reference [6].

3. Results

(1) OH Radicals from Selected Dissociative Recombination Reactions

The first reaction chosen for study was the $HCO_2^+ + e$ reaction. An H_3^+ /electron plasma was created as described above and CO_2 was added to create the HCO_2^+ /electron plasma. As the CO_2 was added, OH(v=0) was immediately detected by the LIF facility; the intensity of the LIF increased, as the flow of CO_2 was increased, reaching a maximum when all the H_3^+ had been converted to HCO_2^+ and all the latter ions had recombined with electrons. To demonstrate conclusively that the OH was indeed produced from HCO_2^+ recombination and to determine f_{OH} , the fraction of OH(v=0) produced per recombining ion, the LIF intensity, I, was determined as a function of the initial (upstream) number density of HCO_2^+ ($=n_e(0)$) using the Langmuir probe. A simple kinetic analysis [6]

shows that a plot of $n_e(0)^2/I$ versus $n_e(0)$ should be linear if the $\text{HCO}_2^+ + e$ reaction is the source of the OH radicals. The slope of the plot provides a value for f_{OH} and the intercept a value for α_e for the reaction. That the α_e for $\text{HCO}_2^+ + e$ obtained by this method agrees closely with the α_e determined by the 'direct method' described above is an excellent check on the validity of the approach and gives credence to the value of f_{OH} obtained (see the Table).

Any $\text{OH}(v>0)$ produced in the recombination reaction survives in the helium carrier gas and is not detected by the LIF experiment as configured. However, the addition of NO to the $\text{OH}(v)$ swarm upstream of the LIF detection point caused an increase in I. This is the result of quenching of $\text{OH}(v>0)$ to $\text{OH}(v=0)$ by the NO. Using this method, the fraction of $\text{OH}(v>0)$ produced in the reaction (see the Table) and also the rate coefficient of the $\text{OH}(v>0) + \text{NO}$ quenching reaction were determined [6]. The $\text{HCO}_2^+ + e$ reaction was then used routinely as a calibration for the LIF intensity when studying the OH produced in other recombination reactions. Thus the f_{OH} for $\text{OH}(v=0)$ and $\text{OH}(v>0)$ have been determined for the recombination of O_2H^+ , H_3O^+ and N_2OH^+ ions (see the Table and references [7,8]). It is worthy of note that radiation emission in the wavelength region near 306 nm was detected from the recombining HCO_2^+ /electron plasma. This has been attributed to the production of electronically excited $\text{OH}(\text{A-state})$ in the recombination reaction (these molecules radiate quickly (in ~ 700 ns) and are detected by the LIF as $\text{OH}(\text{X-state})$ molecules).

(ii) H atoms from Selected Dissociative Recombination Reactions

The fraction of H atoms released per recombining ion, f_{H} , cannot be determined directly by VUV absorption because the H atom number density, $[\text{H}]$, generated is not sufficient to result in an accurately measurable L_{α} absorption. So this had to be carried out, again by converting the H atoms to OH using NO_2 and by exploiting the LIF facility. These studies were also complicated due to the presence of background H atoms generated in the ion chemistry needed to prepare the recombining plasmas. Two different experimental approaches were taken. (i) H_3^+ /electron plasmas were created as described above (i.e. at a helium carrier gas pressure of 1.6 torr) and, as before, MH^+ /electron plasmas were created by the addition of appropriate gases, M. H atoms were present in the carrier gas due to (a) the $\text{H}_2^+ + \text{H}_2 \longrightarrow \text{H}_3^+ + \text{H}$ and the $\text{Ar}^+ + \text{H}_2 \longrightarrow \text{ArH}^+ + \text{H}$ reactions, (b) the recombination of any $\text{H}_3^+(v>3)$ in the gas phase and

$H_3^+(v \geq 0)$ at the walls and (c) from the recombination of MH^+ . To account for the background H atoms due to (a) and (b) and hence to determine f_H due to the reaction $MH^+ + e$ (in (c)), experiments were carried out using an O_2H^+ recombining plasma ($M=O_2$). On addition of O_2 , first $[OH]$, and hence f_{OH} , was determined for the recombination of O_2H^+ . Thus f_{OH} was found to be 0.6 and hence it follows that $f_H = 0.4$ (since if OH is not a product of the recombination reaction, then an H atom must be). Thus on addition of NO_2 to the carrier gas, OH was formed from the H atoms generated by (a), (b) and (c) above, and since (c) is accounted for, the background H atom number density can be deduced. Now other gases, M, were added to generate other MH^+ ions (see the Table) and the f_H were deduced. It must be noted, however, that differential diffusion of H atoms (not destroyed at the walls of the flow tube) and OH radicals (destroyed, in part, at the walls) had to be accounted for. This was achieved by using the $HCO^+ + e \longrightarrow CO + H$ reaction as a calibration, noting that for this reaction $f_H = 1$ and no OH is generated [8]. Using this procedure an effective relative diffusion loss factor of 1.7 was obtained.

(ii) Using method (i), the H atom background was relatively large and so a second method was used to reduce this background. This involved our 'double microwave cavity method' in which a second cavity was used downstream of the cavity which created the plasma. The second cavity was only weakly energised in order to heat away the plasma electrons (and ions) ensuring that He^m are the dominant reactive species downstream. Then the Penning reaction $He^m + CO \longrightarrow CO^+ + e + He$ was exploited to create a CO^+ /electron plasma to which H_2 was added to generate an HCO^+ /electron plasma via the reaction $CO^+ + H_2 \longrightarrow HCO^+ + H$ (i.e. creating only one H atom per ion). The addition of M to these plasmas then created MH^+ /electron plasmas with relatively little H atom background. We also exploited the reaction $He^m + Ar \longrightarrow Ar^+ + e + He$ and used the Ar^+ ions as precursors for some experiments (e.g. $Ar^+ + H_2O \longrightarrow H_2O^+ + Ar$; then $H_2O^+ + H_2O \longrightarrow H_3O^+ + OH$). The f_H were determined by adding NO_2 as described under (i). Thus, using both methods (i) and (ii) the f_H for several reactions were obtained and these, together with f_{OH} , are given in the Table. The details of these experiments and a discussion of the results will be given in a later paper.

4. Concluding Remarks

The results reported here for f_{OH} and f_H are the first ever reported for the dissociative recombination of ground state polyatomic ions. These kind of data are vital if a proper understanding of dissociative recombination and of plasma chemistry are to be obtained. The data obtained to date are of immediate value to interstellar chemistry, as has been discussed in a recent paper [7]. Clearly, the FALP experiments can be extended to determine the f_H for many other ions and also to determine, for example, the f_{CN} for CN-bearing ions (e.g. H_2CN^+ , CH_3CNH^+ , etc.). Such experiments will soon be initiated.

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Table of values of $f_{OH}(v=0)$, $f_{OH}(v>0)$ and f_H . Also included are the f_H data obtained by the Rennes group using their FALP apparatus and VUV absorption to determine f_H directly. For further explanation of f_{OH} , see Reference [6].

Recombining Ion	$f_{OH}(v=0)$	$f_{OH}(v>0)$	f_H B'ham	f_H Rennes
N_2H^+	-	-	1.0	1.0*
HCO^+	0	0	1.0	1.0*
O_2H^+	0.40	0.20	0.40	-
HCO_2^+	0.17	0.17	0.73	0.83
N_2OH^+	0.14	0.17	0.70	0.98
H_3O^+	0.46	0.19	1.0	1.16
$C_2H_5^+$	-	-	1.17	1.35
NH_4^+	-	-	0.86	1.03
H_2CN^+	-	-	0.63	-
CH_3CNH^+	-	-	0.69	-
$OCSH^+$	0	0	-0.1	0.31
H_3S^+	-	-	0.48	0.38
CH_5^+	-	-	1.16	1.19

* Calibration reaction

REFERENCES

1. E. Alge, N.G. Adams and D. Smith, J.Phys.B. 16, 1433, (1983)
2. N.G. Adams, D. Smith and E. Alge, J.Chem.Phys., 81, 1778, (1984)
3. N.G. Adams and D. Smith, Chem.Phys.Lett., 144, 11, (1988)
4. N.G. Adams and D. Smith, in 'Astrochemistry' (eds. M.S. Vardya and S.P. Tarafdar) pl, Reidel, Dordrecht 1987
5. D. Smith and N.G. Adams, in 'Swarms of Ion and Electrons in Gases' (eds W. Lindinger, T.D. Mark and F Howorka) p 284, Springer-Verlag (Vienna) 1984
6. N.G. Adams, C.R. Herd and D. Smith, J.Chem.Phys., 91, 963, (1989)
7. C.R. Herd, N.G. Adams and D. Smith, Ap.J., (1990) in press
8. N.G. Adams, C.R. Herd and D. Smith, in Proceedings of 16th ICPEAC, New York, 1989

APPENDIX 4

SIFT STUDIES OF THE REACTIONS OF
 F^+ , Cl^+ , Br^+ and I^+ AT 300K

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SIFT STUDIES OF THE REACTIONS OF F^+ , Cl^+ , Br^+ AND I^+ AT 300K

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Abstract: The rate coefficients and ion product distributions have been determined for the reactions of F^+ , Cl^+ , Br^+ and I^+ with N_2 , D_2 , H_2 , CO , CO_2 , CH_4 , H_2O , O_2 , C_2H_2 , OCS , C_2H_4 , H_2S , NH_3 , NO and C_6H_6 using the SIFT technique. Several reaction processes are observed and the results are interpreted in terms of the recombination energies of the reactant ions, the ionization energies of the reactant molecules and the available electronic states in the product ions.

1. Introduction

The ground state of the singly-charged atomic halogen positive ions have a $^3P_{2,1,0}$ configuration, the 3P_2 being the lowest energy state. The recombination energies of the 3P_2 states of the ions are $F^+(17.42\text{eV})$, $Cl^+(12.97\text{eV})$, $Br^+(11.81\text{eV})$ and $I^+(10.45\text{eV})$. The large recombination energy of F^+ ions renders charge transfer energetically possible with all molecular gases, whereas charge transfer can only occur between I^+ ions and molecules of low ionization energies. However, when charge transfer cannot proceed, other 'chemical' reactions may occur in the gas phase such as atom abstraction, hydride ion transfer and ion/molecule association; indeed, these processes can occur in parallel with exothermic charge transfer. Clearly, the reaction processes that can or may occur will also depend on the nature of the reactant molecule. Some previous studies have been carried out on the reactions of F^+ , Cl^+ and Br^+ with a number of simple molecules at room temperature [1-4]. We have, however, undertaken a more extensive and systematic study of the reactions in the gas phase of all four atomic halogen ions with some fifteen molecular gases varying in atomicity, ionization energy, bond strengths etc., with a view to elucidate how the ionic and molecular properties determine the course of the reactions.

2. Experimental

The experiments were carried out at 300K using our selected ion flow tube (SIFT) apparatus. The details of the apparatus, the experimental

method and the analysis of raw data to obtain the rate coefficients and ion product distributions have been described in a recent review [5]. It is sufficient to say here that the reactant ions were created in electron impact ion sources (both high pressure and low pressure sources were used) containing an appropriate vapour (CF_3Br for F^+ and Br^+ , CCl_3Br for Cl^+ and CH_3I for I^+) and injected into pure helium carrier gas at a pressure of ~ 0.5 torr in the SIFT. Reactant gases were added in controlled amounts to the reactant ion swarm/carrier gas and the rate coefficients and product ion distributions were determined in the usual way.

3. Results

The fifteen molecular species included in this study ordered in decreasing ionization energy (given in eV in parenthesis) are $\text{N}_2(15.58)$, $\text{D}_2(15.46)$, $\text{H}_2(15.43)$, $\text{CO}(14.01)$, $\text{CO}_2(13.77)$, $\text{CH}_4(12.62)$, $\text{H}_2\text{O}(12.61)$, $\text{O}_2(12.06)$, $\text{C}_2\text{H}_2(11.40)$, $\text{OCS}(11.17)$, $\text{C}_2\text{H}_4(10.50)$, $\text{H}_2\text{S}(10.47)$, $\text{NH}_3(10.15)$, $\text{NO}(9.25)$ and $\text{C}_6\text{H}_6(9.24)$. The rate coefficients and ion product distributions for the reactions of these molecules with F^+ , Cl^+ , Br^+ and I^+ , some sixty reactions, represents a large amount of data which will be reported and discussed in detail in two longer publications [6,7]. Here we summarise the essential features of the data by discussing the reactions of each reactant ion species as a group.

(i) *The F^+ Reactions*

F^+ is a closely spaced triplet with large recombination energies, in eV, $17.42(^3\text{P}_2)$, $17.47(^3\text{P}_1)$, $17.48(^3\text{P}_0)$. Charge transfer is energetically allowed with all the molecules included in the study and this process is observed in every reaction. The reactions are all fast (i.e. the measured rate coefficient, k , is equal to, or close to, the collisional rate coefficient, k_c) except for the CH_4 reaction, for which $k \sim 0.1 k_c$ (see below). That these reactions are so efficient is due to the accessibility of electronic states of the product ions with good Franck-Condon Factors from the ground state of the reactant molecules [8]. Dissociative charge transfer cannot occur in the reactions involving the molecules with large ionization energies and so only the parent positive ions are observed as products (e.g. N_2^+ , CO^+ and CO_2^+). For most of the other reactant molecules, fragmentation of the molecular ions occurs following charge transfer; for example, HS^+ and S^+ (and not H_2S^+) are the

ionic products of the H_2S reaction. The CH_4 reaction is interesting since, as mentioned above, it is slow and a single dissociative product ion, CH_3^+ , is observed. It seems likely that the $\text{F}^+ + \text{CH}_4$ reaction proceeds to a purely electronic repulsive state of CH_4^+ (dissociating to $\text{CH}_3^+ + \text{H}$) or to a fully predissociated state of CH_4^+ .

The NO and O_2 reactions are worthy of special note. Again these reactions are rapid ($k \sim k_c$) and a single product ion is observed in each reaction, i.e. NO^+ and O_2^+ . Since these charge transfer reactions are clearly very exothermic to produce ground vibronic state NO^+ and O_2^+ ions, we surmise that the reactions proceeded to produce $(\text{NO}^+)^*$ and $(\text{O}_2^+)^*$ in metastable electronic states. These metastable ions are known to react with Ar atoms [9] and, thus, using argon as a monitor gas we confirmed that the metastable ions were indeed formed in the F^+ reactions with NO and O_2 .

(ii) The Cl^+ Reactions

Cl^+ is also a closely spaced triplet with energies, in eV, of 12.97 ($^3\text{P}_2$), 13.05 ($^3\text{P}_1$) and 13.09 ($^3\text{P}_0$). Charge transfer is allowed with all the molecules included in the study except for N_2 , D_2 , H_2 , CO and CO_2 , and it is observed when it is energetically allowed, often in parallel with other processes. The reactions with CO and CO_2 result in the production of the association ions $\text{Cl}^+\cdot\text{CO}$ and $\text{Cl}^+\cdot\text{CO}_2$; with D_2 and H_2 the product ions are DCl^+ and HCl^+ . Most of the binary reactions are fast, the major exception being the charge transfer reaction with C_2H_2 which is very slow ($k \leq 0.05 k_c$), and this is interpreted as being due to the poor Franck-Condon overlap between the ground state of the neutral molecule and the accessible vibronic states of the corresponding molecular ion. There is also a propensity for the formation of H-Cl and C-Cl chemical bonds in some of the products of these Cl^+ reactions (for example, H_2Cl^+ and CH_2Cl^+ are products of the $\text{Cl}^+ + \text{CH}_4$ reaction).

(iii) The Br^+ Reactions

The energies of the triplet states of this ion, in eV, are 11.81 ($^3\text{P}_2$), 12.23 ($^3\text{P}_1$) and 12.32 ($^3\text{P}_0$). The smaller recombination energies of these ions ensures that charge transfer can occur with fewer molecules in the list. The O_2 reaction is of interest because the ionization energy of O_2 , which is 12.06 eV, lies between the recombination energies of Br^+ in the $^3\text{P}_2$ and $^3\text{P}_1$ states. Thus charge transfer is not allowed with $\text{Br}^+(^3\text{P}_2)$ whereas it is with the $^3\text{P}_1$ and $^3\text{P}_0$ state ions and then it is

observed to occur rapidly. Charge transfer occurs in most cases when it is allowed but 'chemical reactions' are more evident for Br^+ than for F^+ and Cl^+ . For example, CH_2Br^+ is a product of the CH_4 reaction and BrS^+ is a product of the OCS reaction.

(iv) The I^+ Reactions

The energies of the triplet states of this ion, in eV, are $10.45(^3\text{P}_2)$, $11.23(^3\text{P}_1)$ and $11.33(^3\text{P}_0)$. Charge transfer is thus energetically allowed only with OCS , C_2H_4 , H_2S , NH_3 , NO and C_6H_6 , and with the last four molecules it does occur producing only the parent ions (H_2S^+ , NH_3^+ , NO^+ , C_6H_6^+). C_2H_4^+ is a minor product of the C_2H_4 reaction and, significantly, OCS^+ is a 45% product of the OCS reaction which corresponds to the fraction of the $^3\text{P}_{1,0}$ ions in the I^+ swarm, assuming a statistical weight distribution. The $\text{I}^+(^3\text{P}_2)$ ions cannot charge transfer with OCS but the reaction of ions in this state proceed efficiently to produce IS^+ and CO . The I^+ reactions with CO and C_2H_2 are ternary association reactions producing $\text{I}^+\cdot\text{CO}$ and $\text{I}^+\cdot\text{C}_2\text{H}_2$, the C_2H_2 reaction being particularly efficient.

4. Concluding Remarks

A wide variety of reaction processes are evident in this study of the reactions of singly charged atomic halogen ions. Charge transfer is an important process, exclusively so for the energetic F^+ reactions, and ion/molecule association and 'chemical reactions' occur to a greater extent for the less energetic ions. The details of this extensive study will be reported soon in two major papers [6,7].

References

1. A.S.M. Raouf, J.D.C. Jones, D.G. Lister, K. Birkinshaw and N.D. Twiddy, *J.Phys.B:Atom.Molec.Phys.*, **13**, 2581 (1980)
2. A.B. Rakshit, *Chem.Phys.Letters*, **75**, 283 (1980)
3. M. Hamdan, N.W. Copp, K. Birkinshaw and N.D. Twiddy, *J.Phys.B: Atom.Molec.Phys.*, **17**, 849 (1984)
4. M. Hamdan, N.W. Copp, K. Birkinshaw, J.D.C. Jones and N.D. Twiddy, *Int.J.Mass Spectrom.Ion Phys.*, **69**, 191 (1986)
5. D. Smith and N.G. Adams, *Adv.Atom.Mol.Phys.*, **24**, 1 (1988)

6. C.A. Mayhew and D. Smith, "The Reactions of F^+ ions at Thermal Energies", 1990. In preparation.
7. C.A. Mayhew and D. Smith, "A SIFT Study of the Reactions of F^+ , Cl^+ , Br^+ and I^+ with Several Molecular Gases at 300K", 1990. In preparation.
8. Details on many of the molecules studied here can be found in "Photoabsorption, Photoionisation and Photoelectron Spectroscopy" by J. Berkowitz, Academic Press (1979)
9. J. Glosik, A.B. Rakshit, N.D. Twiddy, N.G. Adams and D. Smith, J.Phys.B:Atom.Mol.Phys., 11, 3365 (1978)

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